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# Combined use of geophysical and geochemical methods to assess areas of active, degrading and restored blanket bog

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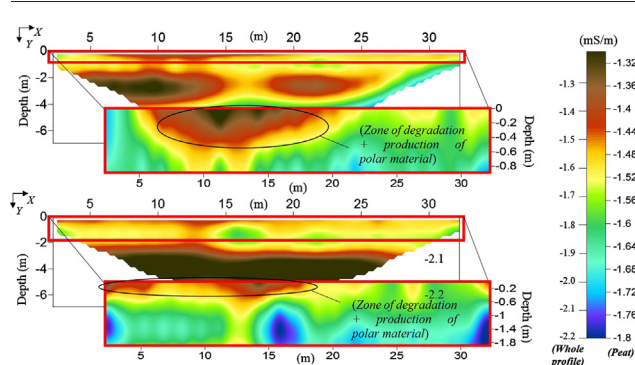
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## HIGHLIGHTS

- Degradation processes alter the normalized chargeability.
- Degrading and restored locations are dominated by vascular plants.
- Vascular plants permit oxygen diffusion via roots deeper into subsurface.
- Aerated conditions support oxidation of phenols and production of C=O double bonds.
- Polar compounds increase normalized chargeability and cation exchange capacity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Here we combine the use of geo-electrical techniques with geochemical analysis of the solid and liquid phase to determine subsurface properties and general peatland health. Active, degrading and restored peat locations were analysed from the same blanket bog site (ensuring they were under the same environmental conditions, such as rainfall and temperature) at the Garron Plateau, Northern Ireland. A normalized chargeability (ratio of resistivity (inverse of conductivity) and chargeability) profile was compared with organic composition analysis of the solid and liquid phases from active, degrading and restored locations. Results show that the degrading location is undergoing high rates of decomposition and loss of organic matter into the interstitial water, whereas the opposite is true for the active location. The restored peat is showing low rates of decomposition however has a high concentration of organic material in the porewater, primarily composing long chain aliphatic compounds, sourced from vascular plants. The ingressions of vascular plants permits the diffusion of oxygen via roots into the subsurface and supports the oxidation of phenols by phenol oxidase, which produces phenoxy radicals and quinones (C=O double bonds). This production of conjugated quinones, which are characterized by a C=O double bond, in the aerated degrading and restored locations, increase the polarity, cation exchange capacity, and the normalized chargeability of the peat. This higher chargeability is not evident in the active peat due to decreased aerobic decomposition and a domination of sphagnum mosses.

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## 1. Introduction

Ombrotrophic peatlands are valuable yet vulnerable ecosystems whose ecology and degradation status are closely linked to the movement and storage of water (Rezanezhad et al., 2016). Actively

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accumulating bogs form natural organic matter (NOM) by the humification of plants under water saturated and anoxic conditions. Drainage introduces oxygen into the previously anoxic environment, causing rapid aerobic decomposition and loss of organic carbon. In addition, drainage can allow the ingress of oxygen to the subsurface promoting aerobic degradation of organic matter. One of the dominant mechanisms proposed for this aerobic degradation is the 'enzymatic latch hypothesis' (Freeman et al., 2001) where the normally constrained phenol oxidase enzyme is able to freely degrade in aerated conditions. The degradation products created by phenol oxidases are phenoxy radicals and conjugated quinones (Sinsabaugh, 2010), which are characterized by a C=O double bond and are electrophilic and polar. The ingress of vascular plants due to overgrazing can also influence oxygen availability and enzymatic activity by allowing oxygen diffusion to deep roots (Romanowicz et al., 2015).

In the 1960's and 1970's, artificial drainage of blanket bogs was introduced across the UK to lower the water table in an attempt to improve agricultural production of the land and to reduce the risk of flooding downstream by creating a moisture deficit (Wallage et al., 2006). It has recently been recognized that these processes have had several negative environmental impacts, including increased downstream flood risk, increased concentrations of organic material in ground and surface water and increased flux of carbon dioxide (CO<sub>2</sub>) to the atmosphere (Holden et al., 2004). In response to these consequences of degradation, many countries are now installing policies that aim to restore a significant portion of peatlands by re-establishing a naturally functioning, actively accumulating system (Emsens et al., 2016). These policies usually involve reducing stocking density for sheep grazing as well as raising the water table by blocking the drains in an attempt to re-create the anoxic conditions necessary for peat accumulation. It is well understood that water table decline within the peat profile, increases rates of decomposition (Wallage et al., 2006), however it is not well-known how rates of humification in drain-blocked areas are affected. Research is now being undertaken to assess the effectiveness of blanket bog restoration (McAnallen et al., 2017). There is a growing recognition that the integration of geophysical measurements into hydrological, process-based watershed studies could significantly advance our understanding of dynamic hydrological processes, especially at intermediate scales, such as in small watersheds to small basins (Robinson et al., 2008). Geophysical studies can be used to improve the understanding of stratigraphy, hydrogeology and hydrochemistry of peatlands (Slater and Reeve, 2002). In particular, near surface geophysics is a strengthening discipline within which hydrogeophysics is emerging, dealing with the application of geophysical methods to investigate subsurface hydrological and microbiological processes (Mendonça et al., 2015a, 2015b).

This study involved comparison between: a drained and over grazed (*degrading*) peat; an actively accumulating (*active*) peat; and a previously drained and overgrazed peat which has undergone drain blocking and reduced grazing (*restored*) from an upland blanket bog catchment in Northern Ireland. The electrical resistivity of the peat subsurface, which is a physical property related to soil type, porosity and the ionic strength of the pore fluid, was measured at each of the three locations (Robinson et al., 2008). Eq. (1) can be used to describe this process which involves placing an array of conductive electrodes into the peat and injecting a current ( $I$ ) into the ground and then measuring the resulting voltage ( $V_p$ ) via potential electrodes (Reynolds, 2011). This response ( $V_p/I$ ) is termed the transfer resistance (through Ohm's law), and is multiplied by a geometric factor ( $K$ ) which accounts for distances and layout of electrodes to calculate the apparent resistivity ( $\rho_a$ ) (Mendonça et al., 2015c).

Apparent resistivity calculation (Reynolds, 2011):

$$\rho_a = \frac{V_p}{I} K(\Omega m) \quad (1)$$

The bulk conductivity is the inverse of resistivity and is also therefore dependent upon soil type, porosity and the ionic strength of the pore

fluid. As resistivity surveys are particularly sensitive to the effects of the fluid conductivity and saturation, Induced Polarization (IP) methods were used as they are more sensitive to the surface chemical properties of the soil (Lesmes and Frye, 2001). Recent research advances in IP (Kemna et al., 2012; Binley et al., 2015; Robinson et al., 2008) have made the technology more attractive for hydrogeophysical research. IP measures the charge loss (chargeability ( $M$ )) of the subsurface material over a given time (Robinson et al., 2008). The response is highly dependent on surface chemistry, which is controlled by charge density, surface area and fluid chemistry (Slater and Reeve, 2002). A measure of the magnitude of the IP effect in the time domain is the chargeability ( $M$ ) (Eq. (2)), where  $V_s$  is the residual voltage recorded within a given time window ( $dt = t_2 - t_1$ ) after which the injection of current was stopped ( $t_1$ ).

Chargeability calculation (Mendonça et al., 2015a, 2015b, 2015c):

$$M = \frac{1}{V_p} \int_{t_1}^{t_2} V_s dt \quad (2)$$

As the resistivity of peat is principally a function of the electrical properties of fluids in the pore space, and chargeability is a function of both the pore fluid electrical properties and those of the interface between the solid matrix and the fluid-bearing pore space, Keller (1959) proposed a normalization of chargeability by calculating the ratio of chargeability to resistivity (Eq. (3)), which Keller termed "specific capacity".

Normalized chargeability calculation (Reynolds, 2011):

$$M_N = M / \rho \quad (3)$$

This normalized chargeability ( $M_N$ ) helps to isolate information about surface chemical processes (Doherty et al., 2010), especially where fluid conductivity ( $\sigma_w$ ) is high (Lesmes and Frye, 2001) and is a better lithologic discriminator than chargeability as it is less influenced by fluid conductivity (Slater and Lesmes, 2002). In the case of peat which has undergone significant aerobic degradation normalized chargeability may be related to the cation exchange capacity of the soils (Revil et al., 2017), in the case of peats it is the negatively charged functional groups that sorb metals (Vile et al., 1999).

Fourier Transform Infrared (FTIR) spectroscopy is a technique which has been widely used to characterise organic matter quality of bulk peat (Holmgren and Norden, 1988) and is capable of distinguishing the principal chemical classes in soil organic matter, such as carbohydrates, lignins, cellulose and proteinaceous compounds, through the vibrational characteristics of their structural chemical bonds (Artz et al., 2008). In particular, FTIR can also identify the presence of C=O compounds such as quinones. Comprehensive Two-Dimensional Gas Chromatography with Flame Ionization Detector (GCxGC-FID) is one of the most powerful tools for environmental analysis of organic compounds in complex matrices and involves splitting a sample injection to two independent gas chromatography columns one of which measures polarity. When the information from the two columns is combined it provides more information about sample constituents than can be observed from a single injection, greatly reducing analysis time (Welke and Zini, 2011).

## 2. Material and methods

### 2.1. The study site

The Garron Plateau (Fig. 1) (latitude 55.003, longitude -6.061) contains the most extensive area of intact blanket bog in Northern Ireland, with an area of over 4650 ha (Joint Nature Conservation Committee, 2016). The peatland complex holds Dungonell reservoir, which is owned by Northern Ireland Water and provides drinking water to the surrounding area. The Garron Plateau peatland is a designated Area of Special Scientific Interest (ASSI), Special Area of conservation (SAC), Special Protection Area (SPA) and a Ramsar site. Although highly protected, previous sampling and analysis undertaken by the Department of

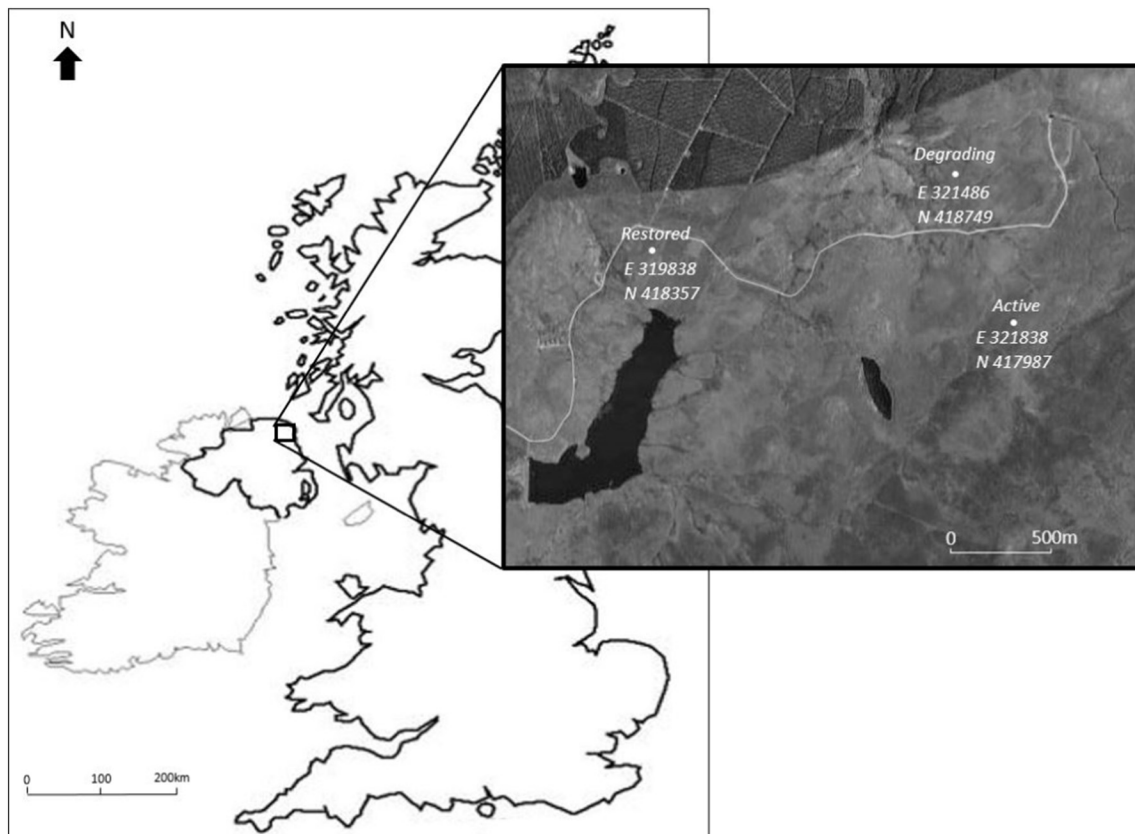


Fig. 1. Location of the Garron Plateau within Northern Ireland.

Agriculture, Environment and Rural Affairs (DAERA) at the site in 2004, determined some areas to be in unfavorable condition, primarily as a result of government incentives in the 1960's and 1970's to drain peats for agricultural purposes. This condition assessment involved a visual inspection of the site using a combination of aerial photography (for locating drains, erosion gullies or land susceptible to erosion), estimation of plant cover in  $2 \times 2$  m plots and condition assessment structured walks (McKeown and Corbett, 2015). Since this condition assessment some of the less-degrading and damaged areas have been re-wetted in an attempt to restore the peat back to health. The restoration programme was started in 2013 and completed in 2014, and covered an area of over 2000 ha of peat (RSPB, 2012). This site is useful for analysis and comparison in that it is extensive (4650 ha) and contains areas of actively accumulating, actively degrading and restored peat in one location. Using the previous condition assessment undertaken by the DAERA, the Royal Society for the Protection of Birds (RSPB) reported the estimated area of the active, degrading and restored locations to be approximately 1005.79, 289.76 and 633.39 ha, respectively (Burns, 2011).

Using the prior knowledge of condition assessment undertaken by DAERA, an area was chosen from within each of the three locations (active, degrading and restored) for analysis. A  $20 \text{ m} \times 20 \text{ m}$  sample grid with was created within each location (McAnallen et al., 2017). The sample grid followed British Geological Survey G-BASE TELLUS Survey Protocol (Johnson, 2005). Near surface 2D Electrical Resistivity Tomography (ERT) and Induced Polarization (IP) profiles were then acquired along a diagonal transect (from sample points 1–3) (Fig. 2) at each of the three locations.

## 2.2. Near-surface geophysical techniques

Non-intrusive geophysical analysis was undertaken to give a detailed understanding of the processes occurring at each area. Near-surface resistivity and IP measurements were undertaken using an IRIS SYSCAL

Pro system ([www.iris-instruments.com](http://www.iris-instruments.com)). The transect was carried out diagonally on each sample grid using an array of 24 electrodes (here we used stainless steel) spaced 1.5 m apart, in the dipole-dipole configuration. IP measurements were acquired using a pulse duration of 2000 ms. Modelling of the resistivity and IP data was carried out using the 2D finite difference inversion program RES2DINV (Loke, 1999). Inversions typically converged within five iterations with a root mean square error of  $<1.71\%$ . Resistivity and Induced Polarization sections

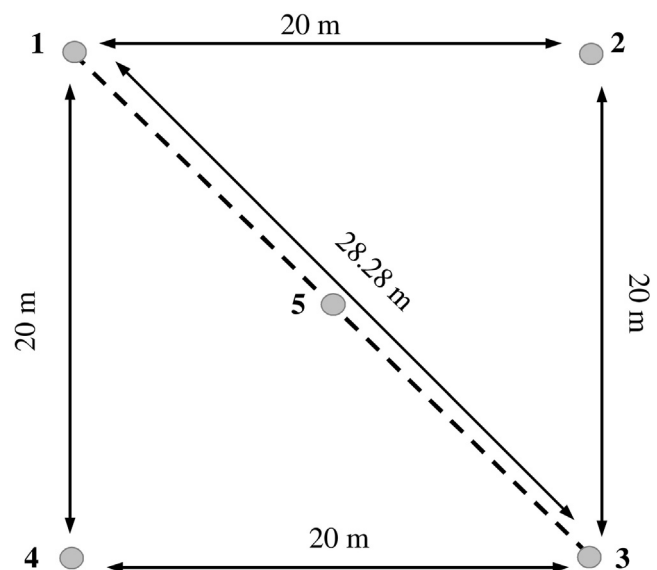


Fig. 2. Sampling grid with transect location marked by a dashed line.



were visualised and interpreted using Surfer software (<http://www.goldensoftware.com/products/surfer>).

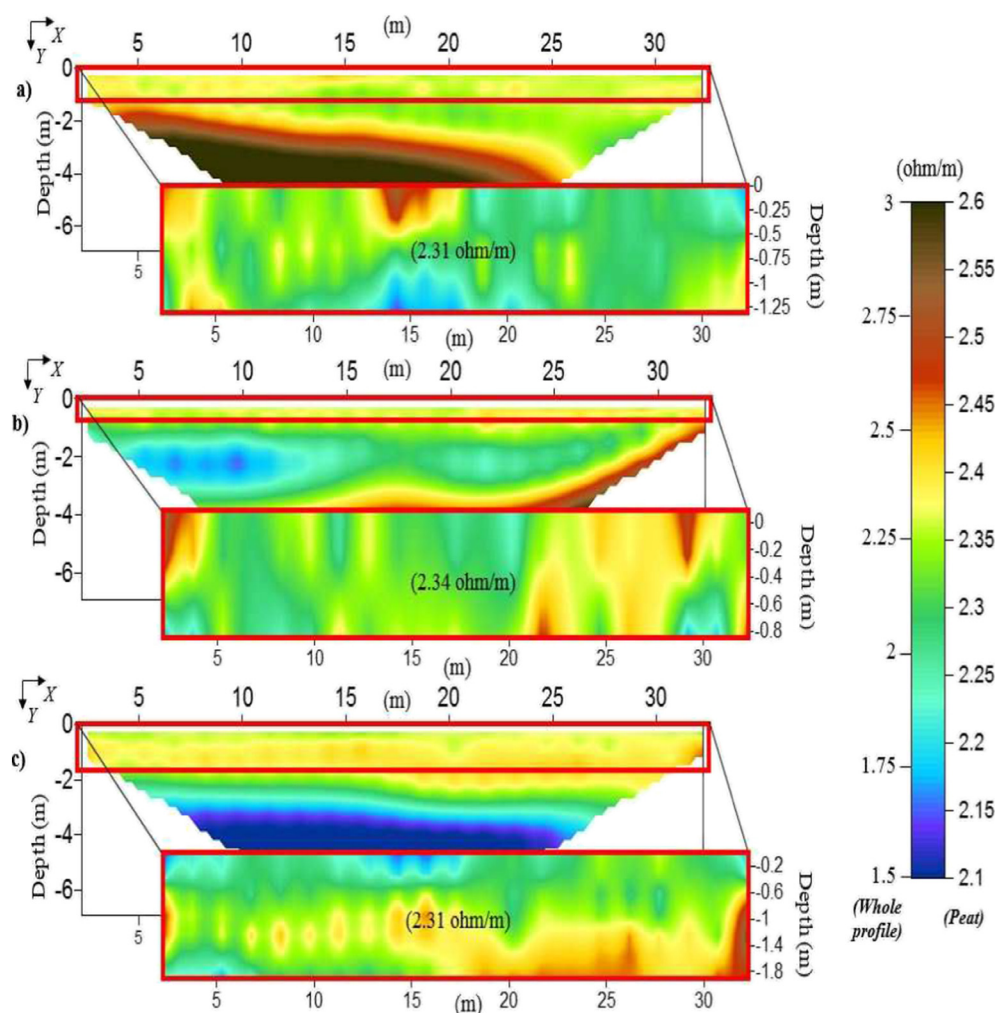
### 2.3. Chemical analyses

After geophysical analysis, peat and porewater samples were collected from each sample location (1–5) from each area (active, degrading and restored). As the location of the water table in relation to the peat surface is an important factor in the biogeochemical processes that occur in the peat, solid samples were also taken at depths of 5, 15, 25 and 35 cm below ground level for FTIR analysis (giving 20 samples from each area (60 in total)). A depth of 35 cm was chosen as in a typical year it is known that in general, a peatland water table fluctuates within the top 30 cm of the peat (Shi et al., 2015). It has been recognized (Esmeijer-Liu et al., 2012) that the top 0 to  $\pm 10$  cm contains the youngest peat which is under aerobic conditions and from 20 + cm is where stability of the catotelm begins. The zone in between (10–20 cm) is where water table fluctuation and catotelm immobilisation is thought to occur (Esmeijer-Liu et al., 2012). The solid samples were collected using a Russian style peat auger which was inserted vertically into the peat layer at each sample location and placed into air-tight sealed sample bags. Porewater samples were collected from each sample location (1–5) within the three areas (active, degrading and restored) using a peristaltic pump and placed into amber glass bottles from the same locations, post core collection for GCxGC-FID analysis. The pore water samples were collected approximately one hour after core collection

to minimise the effects of the disturbance and to allow the water table to settle. All samples were taken back to the lab in low temperature (approx. 4 °C) cooler boxes.

The solid peat samples were air-dried in an oven at a continuous temperature of 28 °C (ensuring minimal loss of volatile organic material) to remove the water and then freezer-milled to a fine powder using a SPEX CertiPrep cryogenic freezer mill 6850. The dried and powdered peat from each location was then analysed using FTIR to determine the organic matter composition at different depths. The spectral characterization of the peat samples was obtained with a Jasco FT/IR-4100 at a scan range of 4000–650  $\text{cm}^{-1}$  and a resolution of 4  $\text{cm}^{-1}$ . Each sample was analysed in triplicate and an average taken to ensure precision. A background reading was also taken between each sample to ensure results did not deviate due to any atmospheric changes within the lab. Although peat samples were collected here, less invasive equipment was used (hand trowel), and only at shallow depths, so as to minimise any long-term disturbance to the peat.

It is known that water exchanges (movement and storage) between wetland sediments and other water bodies can have an important influence upon hydrological, microbiological and chemical processes within the wetland (SurrIDGE et al., 2005; Rezanezhad et al., 2016). It is known that organic matter in both solid and dissolved states has a large specific area and elevated negative charge (Séguin et al., 2004), therefore influencing the electrical conductivity and chargeability values. As mentioned, porewater samples (c. 200 ml) were collected into amber glass bottles at each location so that the organic material within the



**Fig. 3.** Bulk electrical resistivity sections of whole profile as well as close up of the peat layer only at (a) active, (b) degrading and (c) restored locations. NB data are plotted on a log scale. Average conductivity values for the peat are also given in brackets.

interstitial water could be analysed via GCxGC-FID. GCxGC-FID was used to determine the quality of organic material being leached from the peat and was performed using an Irish National Accreditation Board (INAB) accredited method of banding of aliphatic and aromatic hydrocarbons by Complete Laboratory Solutions (CLS) in Ros Muc, Galway, Ireland.

### 3. Results and discussion

#### 3.1. Near surface geophysical analysis

The electrical resistivity survey taken across each location indicates that the peat is shallowest in the degrading location (Fig. 3b) with a thickness of approximately 0.8 m, whereas the restored location (Fig. 3c) is the deepest, with a thickness of approximately 1.8 m. Both these locations are underlain by a layer of clay (thin layer (2 m thick) between 5 and 15 m in the x direction of the degrading location and across the entire transect of restored from 3 mbgl), whereas the peat in the active location (Fig. 3a) is approximately a minimum of 1.25 m in thickness and overlies the resistive basalt bedrock (McKeown and Corbett, 2015). When focusing on the resistivity of the peat layer only, all three locations (Fig. 3) have similar resistivity values (2.31  $\Omega/\text{m}$  for active and restored and 2.34  $\Omega/\text{m}$  for degrading). Although there is a low resolution of the data at the surface as a result of the relatively large spacing between electrodes, (which we suggest should be decreased for future work), we expected to see greater differences in IP sections.

Fig. 4 indicates the chargeability profiles at each location. Chargeability is a function of both the pore fluid electrical properties and those of the interface between the solid matrix and the fluid-bearing pore space within it in the absence of continuous electronic conductors (Slater and Lesmes, 2002). The peat layer in the degrading location (Fig. 4b) has the highest average chargeability of 7.11 mV/V, whereas the active (Fig. 4a) and restored (Fig. 4c) locations have similar average chargeabilities of 5.13 and 5.72 mV/V, respectively. The higher average chargeability in the degrading peat (Fig. 4b) is attributed to the zone of particularly high chargeability at 7–17 m in the x direction, to a depth of 0.3 mbgl.

Although chargeability (Fig. 4) is a physical property related to conductivity/resistivity (Fig. 3), it is highly complex as it is dependent on the bio-geochemical transformations occurring in the subsurface (Binley et al., 2015). The normalized chargeability (Fig. 5) is a direct measure of polarization strength and is less influenced by fluid conductivity (Slater and Reeve, 2002). The peat in the degrading location has the highest average conductivity of 2.34  $\Omega/\text{m}$  (Fig. 3b), highest chargeability of 7.11 mV/V (Fig. 4b) and therefore the highest average normalized chargeability of 0.33 mS/m (Fig. 5b). As with resistivity (Fig. 3), both the active and restored locations have similar normalized chargeability values of 0.025 and 0.029 mS/m, respectively (Fig. 5a and c). The degrading (Fig. 5b) and restored (Fig. 5c) locations have an upper polarizable layer (top 30 cmbgl in degrading and top 20 cmbgl in restored). The active location (Fig. 5a) seems slightly more homogenous and is less polarizable. Both the degraded and restored locations within the

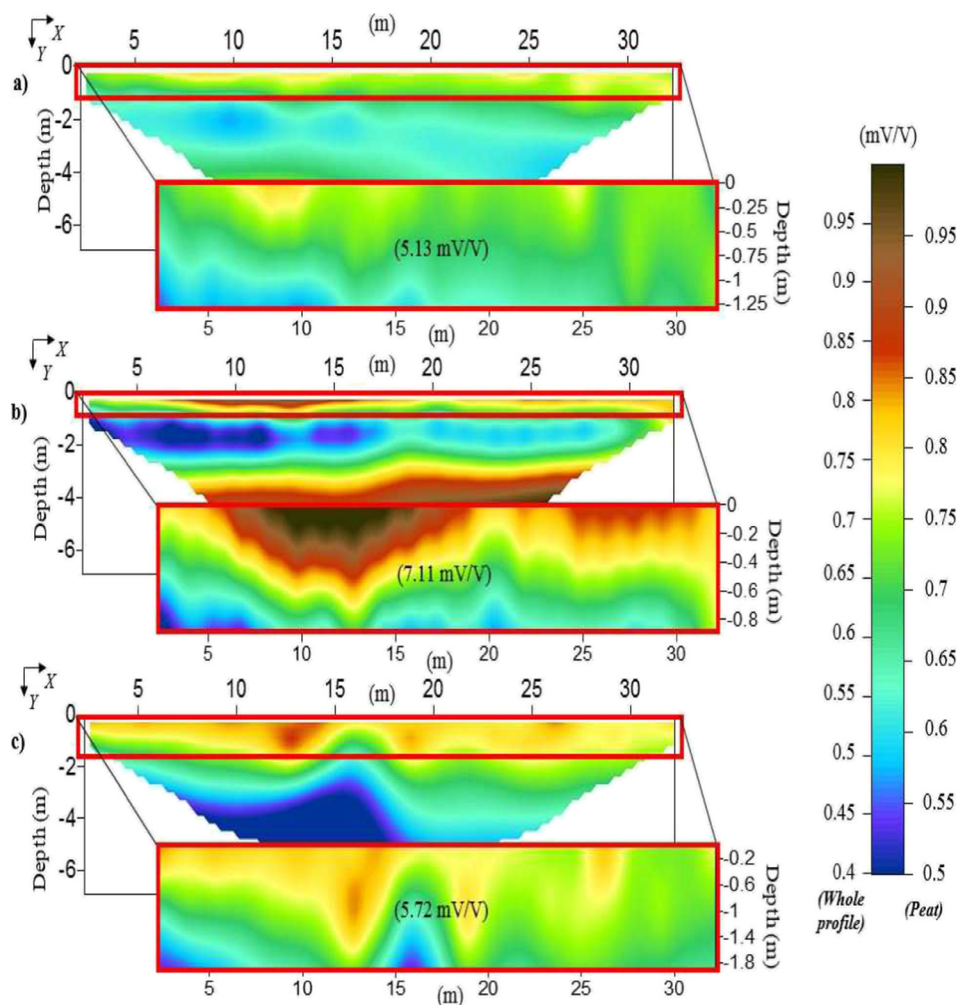
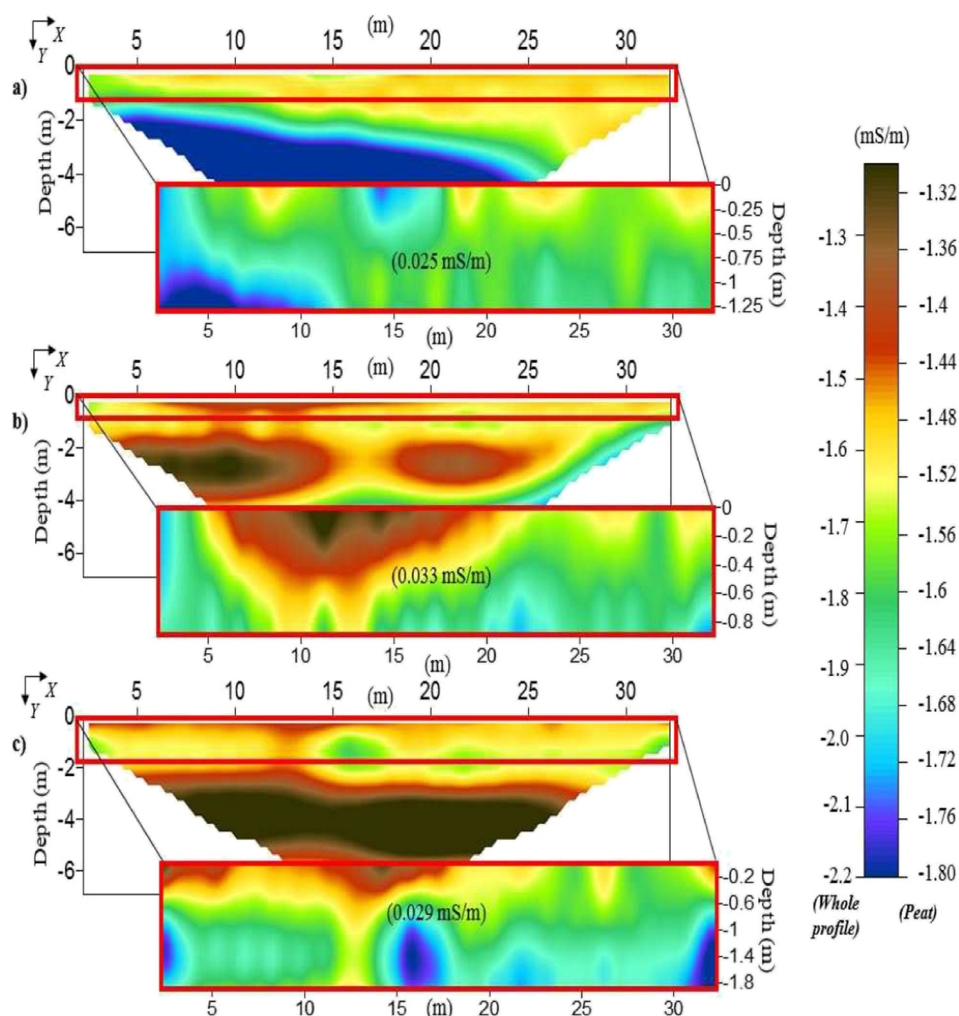


Fig. 4. IP sections of whole profile as well as close up of the peat layer only at (a) active, (b) degrading and (c) restored locations. NB data are plotted on a log scale. Average chargeability values for the peat are also given in brackets.



**Fig. 5.** Normalized chargeability ( $M_N$ ) of sections of whole profile as well as close up of the peat layer only at (a) active, (b) degrading and (c) restored locations. NB data are plotted on a log scale. Average chargeability values for the peat are also given in brackets.

1–2 m show increased levels of normalized chargeability when compared with active location suggesting that the peat close to surface had been altered due to degradation processes.

### 3.2. Chemical analyses

#### 3.2.1. Solid phase

The botanical composition and the degree of humification of peat have a strong influence on the electrical properties of the material (Ponziani et al., 2011). The FTIR spectra of the peat samples (Fig. 6) exhibited typical peaks described for other peatlands, summarized by (Artz et al., 2008).

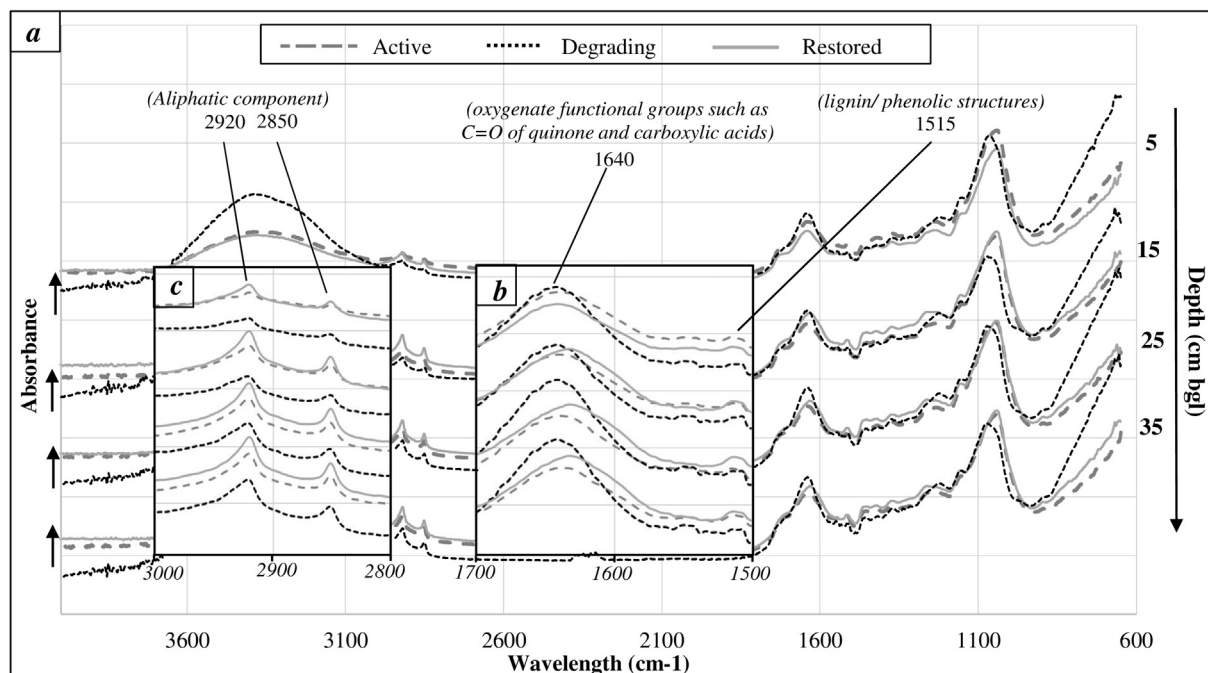
The decomposition of organic material present in the peat samples tends to lead to the formation of phenolic structures derived from lignin ( $1515\text{ cm}^{-1}$ ) as they are more resistant to degradation (Romão et al., 2007). Phenol oxidase is one of the few enzymes able to degrade recalcitrant phenolic materials such as lignin (Freeman et al., 2004). As it requires bimolecular oxygen for its activity, anoxic conditions mean that phenolic compounds ( $1515\text{ cm}^{-1}$ ) accumulate as phenol oxidase activity is suppressed (Freeman et al., 2012). Where oxygen is present however, quinones are produced during the enzymatic oxidation of phenols (Gauillard et al., 1993). Quinones can be identified using FTIR at peaks between  $1700$  and  $1600\text{ cm}^{-1}$  (Bozzolo et al., 2017) and have been found to be present in peat samples at  $1651\text{ cm}^{-1}$  (Bozzolo et al., 2017) and  $1625\text{ cm}^{-1}$  (Delicato, 1996). Fig. 7 indicates the intensity of absorbance of (a) phenolic compounds ( $1515\text{ cm}^{-1}$ ) and (b) C=O

double bonded compounds (quinones) (found here to be at  $1640\text{ cm}^{-1}$ ) wavelengths at each location.

The intensity of the absorption bands depends on the amount of absorbing functional groups and so larger contents of functional groups result in greater intensity of the corresponding absorption bands, whereas smaller contents result in less intensity. The absorbance associated with phenolic compounds at  $1515\text{ cm}^{-1}$  (Fig. 7a) indicate that the degrading location has the lowest concentration whereas the restored has the highest below 15 cm and the active has the highest at 5 cmbgl. The restored location has a lower absorbance at 5 cmbgl which may be as a result of short-term water table level fluctuations increasing decomposition as the presence of bimolecular oxygen activates phenol oxidases, meaning that although elevated, it may not be stable. The absorbance associated with quinones (Fig. 7b), which are produced as a result of the breakdown of phenolic compounds by phenol oxidase, shows that the absorbance is highest in the degrading location, and lower in the active and restored locations. In addition to this FTIR data being used to show the higher rates of decomposition in the degrading location, the degradation of phenolic compounds and subsequent production of C=O double bonds (quinones) can be used to improve the knowledge of the geoelectrical response of the peat (chargeability). These compounds are characterized by a C=O double bond and may therefore result in a higher chargeability, as observed in Fig. 4.

During decomposition, labile compounds are preferentially decomposed while refractory aromatic or aliphatic compounds become enriched (Biester et al., 2014). Fig. 8 indicates the absorbance of aliphatic





**Fig. 6.** (a) Averaged raw solid spectral results calculated from the triplicate spectral values from each location (b) Close up of data from 1500 to 1700  $\text{cm}^{-1}$  (c) Close up of data from 2800 to 3000  $\text{cm}^{-1}$ . Relevant peaks are indicated and their assignment which has been adapted from (Artz et al., 2008). (N.B. results were off-set and overlaid only for visual clarity). Relevant peaks are also indicated.

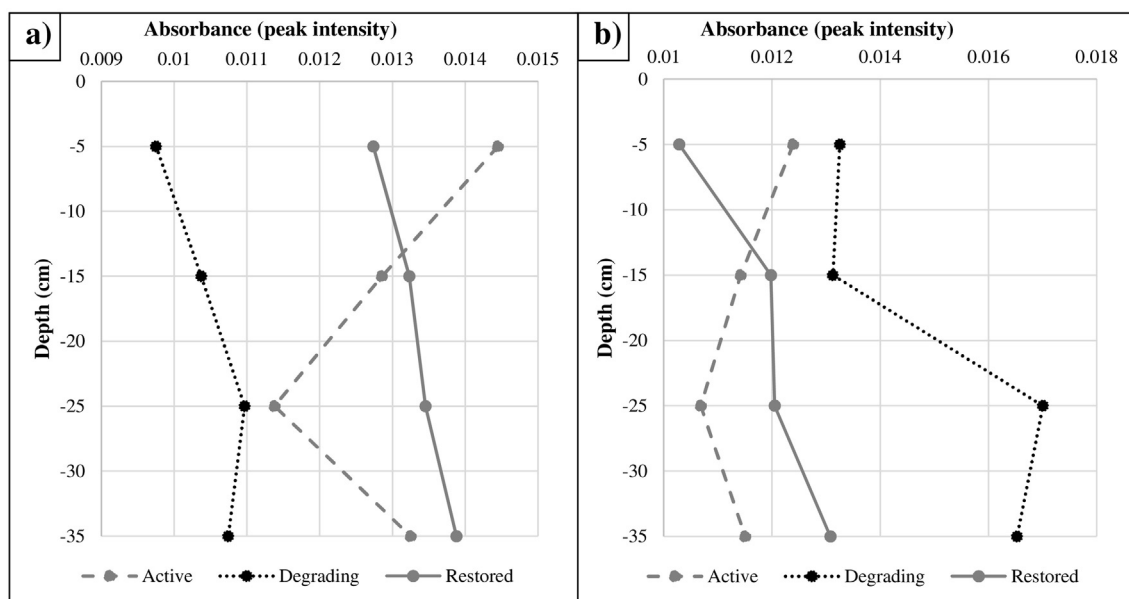
bands at (Fig. 8a) 2920 and (Fig. 8b) 2850  $\text{cm}^{-1}$ . The results show that at each location, the intensity increases with depth, which is expected as humification increases with depth. However, results also show that the active and restored locations have the highest intensity, whereas the degrading location has the lowest absorbance, meaning a higher proportion are being broken down and decomposed here.

### 3.2.2. Liquid phase

Although solid phase organic matter analysis via FTIR has been useful to show the organic composition of the solid peat, GCxGC-FID analysis of porewater has the ability to determine the composition of the organic

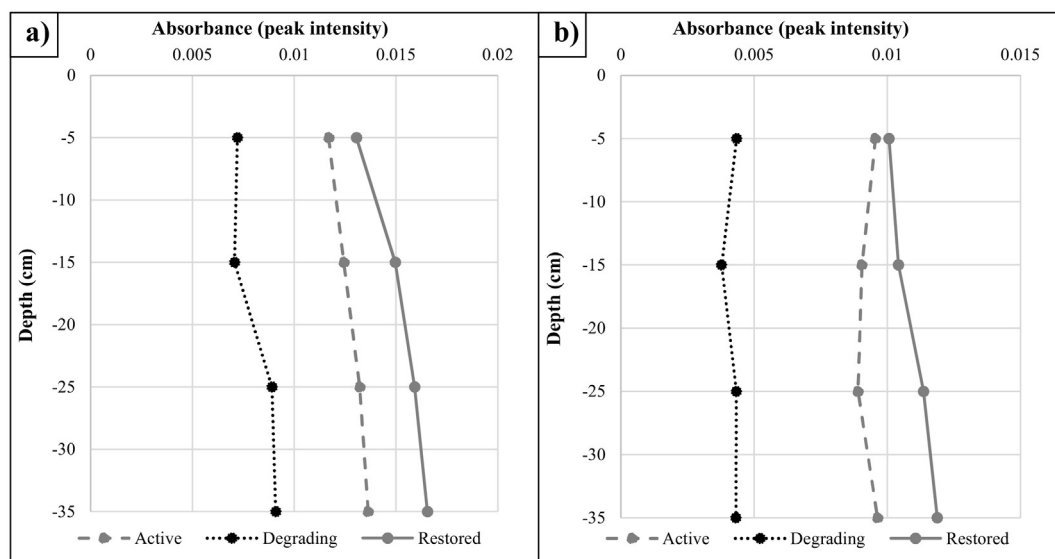
material dissolved in the interstitial water at each location. Table 1 identifies the total aliphatic and aromatic fractions by GCxGC-FID.

The results from Table 1 show that at each location, the concentration of aliphatic compounds is much higher than aromatic components due to oxygenation and decomposition of organic material. The results show that the degrading location is leaching the highest concentration of organic material (3274.23 mg/l) into the surrounding porewater, whereas the active is releasing the least (616.39 mg/l), which further suggests higher rates of peat decomposition and loss of material in the degrading location and a closed, more stable system in the active location. This corresponds with the FTIR data from Fig. 8 whereby the



**Fig. 7.** Average peak intensity values for (a) phenolic compounds (1515  $\text{cm}^{-1}$ ). Calculated standard error was no greater than 0.0074 which occurred at 5 cmbgl in the active location. (b) C=O double bonds (quinones) (1640  $\text{cm}^{-1}$ ) at each location. Calculated standard error was no greater than 0.0016 which occurred at 15 cmbgl in the degrading location.





**Fig. 8.** Average peak intensity values for aliphatic compounds at (a)  $2920\text{ cm}^{-1}$ . Calculated standard error was no greater than 0.0014 which occurred at 25 cmbgl in the degrading location. (b)  $2850\text{ cm}^{-1}$  at each location. Calculated standard error was no greater than 0.0016 which occurred at 25 cmbgl in the degrading location.

degrading material was losing aliphatic compounds from the solid peat. Table 1 also shows that the restored location is still releasing a considerable concentration (1870.53 mg/l) of material into the interstitial water, of which 1388.31 mg/l are from the aliphatic fraction. This aliphatic fraction was therefore analysed further (Fig. 9).

Table 1 indicates that all locations are releasing longer chain length homologues ( $C_{21}$ – $C_{35}$ ), however this is most apparent in the degrading and restored locations. These aliphatic components can be broken down and analysed further to determine the origin of the organic material within the porewater. It is known that different plant types produce leaf wax *n*-alkanes with differing carbon chain lengths (Nichols et al., 2006). In particular, Nichols et al. (2006) found that leaf wax from vascular plants is dominated by  $C_{29}$ – $C_{31}$  *n*-alkanes, whereas sphagnum leaf wax is characterized by  $C_{23}$ – $C_{25}$  *n*-alkanes. *N*-alkanes are produced in variable quantities by plants, and due to their resistance to degradation and early diagenetic alteration, preserve the history of the lipid input (Street et al., 2013), allowing them to be used as biomarkers of palaeoenvironmental changes. A ratio (Table 2) was therefore created between the occurrence of *n*-alkanes derived from vascular and sphagnum input at each location.

The ratio for the active location (Table 2) has the lowest value of 0.39, which indicates a strong predominance of sphagnum input. The degrading and restored locations are suggested to be vascular

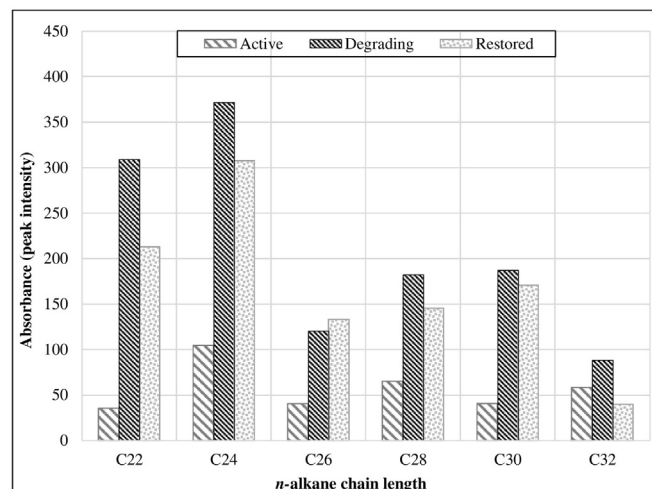
dominated, particularly the restored location, which has the highest ratio value. These results also agree with previous stable isotope analysis undertaken at the site (McAnallen et al., 2017) that found that ingress of vascular plants in the degrading peat profile and the top 15 cmbgl of the restored location has depleted  $^{13}\text{C}$  in the peat. This ingress of vascular plants can therefore influence the oxygen availability through enzymatic activity and allow oxygen diffusion to deep roots (Romanowicz et al., 2015). The consequential breakdown of phenolic compounds during this degradation results in the creation of phenoxy radicals and conjugated quinones (Sinsabaugh, 2010), which correspond to the FTIR analysis in Fig. 7. These compounds are characterized by a  $\text{C}=\text{O}$  double bond which may control the cation exchange capacity and may therefore result in a higher normalized chargeability (Revil et al., 2017), as observed in Fig. 4.

#### 4. Conclusions

The various analyses undertaken throughout this project at the three locations have shown that there is considerable evidence that the restoration project at the Garron has decreased rates of decomposition and improved the quality of the peat. Comparing organic composition

**Table 1**  
Analysis of organic fractions and bandings from porewater samples at each location.

Banding	Fractions	Active (mg/l)	Degrading (mg/l)	Restored (mg/l)
$C_8$ – $C_{10}$	Aliphatic	53.67	39.93	1.67
	Aromatic	0	0	0
$C_{10}$ – $C_{12}$	Aliphatic	10.85	53.31	0
	Aromatic	321.77	439.18	384.07
$C_{12}$ – $C_{16}$	Aliphatic	0	0	0
	Aromatic	0	0	0
$C_{16}$ – $C_{21}$	Aliphatic	0	308.50	0
	Aromatic	0	0	0
$C_{21}$ – $C_{35}$	Aliphatic	230.10	2302.08	1386.64
	Aromatic	0	131.23	0
$C_{35}$ – $C_{44}$	Aliphatic	0	0	0
	Aromatic	0	0	98.15
Total	Aliphatic	294.62	2703.82	1388.31
	Aromatic	321.77	570.41	482.22
	<b>Aliphatic + Aromatic</b>	<b>616.39</b>	<b>3274.23</b>	<b>1870.53</b>



**Fig. 9.** GCxGC-FID breakdown of the aliphatic fraction in porewater samples.

**Table 2**Vascular/sphagnum ratio of *n*-alkane input calculated from Fig. 9.

	Vascular/sphagnum ratio ( $C_{29}-C_{31})/(C_{23}-C_{25})$
Active	0.39
Degrading	0.50
Restored	0.56

analysis between the solid and liquid phases have shown the degrading location to be the most decomposed and actively leaching a high concentration of aliphatic compounds into the surrounding porewater. The opposite was true for the active location, which was shown to have low decomposition rates and low concentrations of organic material in the porewater, indicating a more stable and closed system. The restored location has shown lower rates of decomposition than the degrading peat, however there are still issues with the high concentration of organic material in the pore water in the restored location, which is postulated to be resulting from an ingress of vascular plants due to overgrazing. These vascular plants allow diffusion of oxygen deeper into the subsurface via their roots which permits the degradation of phenol by phenol oxidase. It is postulated that this production of conjugated quinones, which are characterized by a C=O double bond, in the aerated degrading and restored locations, increase the polarity, cation exchange capacity, and the normalized chargeability of the peat. This higher chargeability is not evident in the active peat due to decreased rates of decomposition and a domination of sphagnum mosses. It is proposed that future work at the site should involve more detailed geophysical analysis using an increased number of electrodes with a more refined spacing to better observe the changes in the first 50 cm of peat, as well as more detailed chemical analysis of the solid phase in order to understand this high chargeability, particularly in the degrading location. As normalized chargeability depends linearly on the cation exchange capacity and specific surface area (Revil et al., 2017), and the production of negatively charged functional groups during decomposition results in greater adsorption of positively charged metals, further lab and field scale analysis may provide valuable information on the mechanisms of normalized chargeability of peat following drainage and restoration. Nonetheless, this project has compared how the combined use of geophysical techniques with chemical analysis in the solid and liquid phase can be used well together to assess peatland health.

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